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AN EVALUATION OF GRENVILLE SLATE/MARBLE MIXTURES FOR ALKALI-RESISTANT FIBRE PRODUCTION

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The Production of Specialized Mineral Fibres

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AN EVALUATION OF GRENVILLE SLATE/MARBLE MIXTURES FOR ALKALI-RESISTANT FIBRE PRODUCTION

by

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SUMMARY

Melting points, melt viscosities and alkali-resistance were measured for Grenville slate, and five mixtures with marble to evaluate their potential for alkali-resistant fibre production. Mixture compositions range from 40 to 80% slate. Melting points, varying from 1220 to 1385 °C, are relatively low. The viscosity results indicate that 3 mixtures ranging from 80% slate/20% marble to 60% slate/40% marble are in the viscosity range suitable for fibre formation by spinning or blowing and that slate sample with high viscosities can be converted into fibres by a continuous drawing method. All six glass samples show much higher alkali-resistance than soda-lime glass. The 70% slate/30% marble sample provides the greatest alkali-resistance but it is still less than high zirconia-containing glass and Vermont slate glass. The combination of high SiO_2 and Fe_2O_3, and low Al_2O_3, CaO and MgO contents could be the cause for the less alkali-resistance.

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INTRODUCTION

Many attempts have been made to produce alkali-resistant glass fibres to replace asbestos as reinforcement in cement. One such fibre was made from a 50/50 mixture of limestone and Vermont slate at the University of California, Los Angeles (1). This fibre was claimed to show alkali-resistance superior to the commercial available high zirconia-containing fibres which are far more expensive to produce. In view of this, Dr. J. Springer of Ontario Ministry of Natural Resources approached CANMET to evaluate Grenville slate and its mixtures with marble as raw materials for producing alkali-resistant fibres. Since this was in line with a CANMET's project - The Production of Specialized Mineral Fibres, this slate was included in the study.

EXPERIMENTAL WORK

The evaluation work was carried out as follows:

1. determine the sample mix proportioning of the raw materials according to the chemical analysis data,

2. measure the melting point of the charge mixtures,

3. measure the viscosities of the molten charge mixtures,

4. determine the alkali-resistance of the glass samples.

SAMPLES

Table 1 lists chemical compositions of the slate and marble, and mix proportioning and calculated compositions of the five mixtures.

Table 1. Chemical compositions and melting points of samples

Sample	Mix proportion		Wt %									M.P.
	Wt % Slate	Wt % Marble	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	Na_2O	TiO_2	MgO	LOI	°C
Slate	100	-	65.5	14.6	9.82	0.26	3.77	0.21	1.59	1.38	2.60	1385
Marble	-	100	2.62	0.61	0.24	55.9	n.a.	n.a.	n.a.	0.91	42.11	n.d.
Mix 1	80	20	60.0	12.8	8.6	12.4	3.3	0.2	1.4	1.4	-	1265
Mix 2	70	30	54.2	12.1	8.1	19.7	3.1	0.2	1.3	1.4	-	1220
Mix 3	60	40	49.0	11.0	7.3	27.3	2.7	0.2	1.2	1.4	-	1235
Mix 4	50	50	43.3	9.7	6.4	35.7	2.4	0.1	1.0	1.5	-	1238
Mix 5	40	60	37.1	8.3	5.4	44.9	2.0	0.1	0.6	1.5	-	1268

LOI - Loss on ignition
n.a. - not analyzed
n.d. - not determined

A Leitz heating microscope, type II A-P, was used to determine the melting points of the various samples, and photomicrographs, shown in Fig. 1, were taken during the heating of a small specimen in air. The shrinkage and change in the image of the specimen indicate the thermal behaviour of the sample. The measured melting points, shown in Table 1, are relatively low with the highest for the slate at 1385°C and the lowest for Mix 2 (70% slate/30% marble) at 1220°C. Thus all samples should melt easily.

VISCOSITY MEASUREMENT

Melt viscosity is an important factor in determining the convertibility of the melt into fibres and the quality of the formed fibre. Viscosity measurements were carried out by CANMET's high temperature viscometer.

Viscometer and Measurement Procedure

The high temperature viscometer system is shown schematically in Fig. 2. It consists of (a) an induction furnace (b) a viscometer incorporating a variable speed Brookfield torque meter with a molybdenum crucible and bob

and (c) a gas train. Details of the apparatus construction are given elsewhere (2).

Induction heating is used to melt the sample by coupling an induction generator to the molybdenum crucible. The heat loss from the furnace is minimized by placing the molybdenum crucible inside an alumina crucible, the gap between the two crucibles being filled with zirconia grains as insulation. In addition, an alumina tube lined with molybdenum foil is used as a heat shield, and a molybdenum heat reflector plate is placed on top of the alumina tube. The whole assembly is set inside a silica tube which, in turn, is snuggly fitted inside the induction coil.

The torque meter is a Brookfield Rheolog type viscosity transmitter, Model RVG, equipped with an 8-speed transmission. The Rheolog sensing head (transmitter) output is fed into a pneumatic - to - electric transducer giving an output of 0-10 mv which, in turn, is fed to a recorder. The viscometer system is calibrated using standard silicone oils. The signal from the transmitter is recorded in terms of millivolts for a given bob rotation speed for each standard viscosity fluid.

The viscosity measurements are carried out under a positive pressure of argon mixed with 10% nitrogen. The nitrogen serves to eliminate the ionization (arcing) of the argon gas at high temperature.

About 130 g of sample are required for each determination, the sample being calcined at 1000°C before viscosity measurements are made. After the sample-filled molybdenum crucible has been properly positioned in the induction furnace, the system is flushed with argon gas for about 5 min. The furnace temperature is then raised to the desired minimum for the viscosty measurement. Once the furnace has reached thermal equilibrium, the bob is lowered into the melt and the torque meter motor started. Viscosity readings are recorded continuously as the furnace temperature is increased to a maximum of 1650°C. The melt temperature is monitored simultaneously by an optical pyrometer through a viewing window. The melt is cooled and viscosity readings taken until a crust appeared on the melt. The melt is then quick-frozen by flushing argon gas through the silica tube assembly.

ALKALI-RESISTANCE TESTS

Alkali-resistance tests were carried out by the following procedure:

1. The frozen glass sample from the viscosity measurements is crushed, ground and screened. The portion of minus 600 plus 425 μm is retained for leaching tests.

2. Three g of the graded glass is placed in a 500 mL plastic bottle with 150 mL of 10% NaOH (15 g NaOH dissolving in 150 mL distilled water). The bottle is capped and the cap attached to a motor-driven shaft.

3. The bottle is submerged in a constant-temperature bath at 60°C. The sample and the solution are constantly stirred by rotation of the motor-driven shaft for a leaching period of 6 or 24 h.

4. At the end of the leaching period, the glass sample is filtered, washed with distilled water, dried and weighed and the weight loss calculated.

For comparison study, a high zirconia-containing glass was prepared with the composition of SiO_2 72.9%, Al_2O_3 1.8%, ZrO_2 15%, Na_2O 11.1% and Li_2O 1.0% which is similar to the pioneered alkali-resistant zirconia fibres produced at Building Research Station in the U.K. Both this zirconia glass and a lime-soda glass sample obtained by crushing waste glass bottle were subject to the same alkali-resistance tests.

RESULTS

VISCOSITIES

The melt viscosities for the slate and the five sample mixtures are presented individually as a function of temperature in Fig. 3-8. Viscosity decreases as temperature increases and as the marble content in the mixture increases. An increase in temperature causes progressive loosening of the silicate network structure by thermal agitation. The major component in

marble is CaO which is a silicate network breaker. An increase of marble content breaks down the silicate structure and decreases the average size of the silicate anions. This silicate network size decrease is reflected by the viscosity decrease.

Zhilin observed that a good quality mineral wool was obtained by the spinning or blowing method when the melt viscosity ranged from 0.5 Pa.s (500 centipoise) to 1.5 Pa.s (1500 centipoise) at 1500°C and 1400°C respectively (3). This was confirmed by previous work (4). The viscosity data indicate that mixtures 1 (80% slate/20% marble), 2 (70% slate/30% marble) and 3 (60% slate/40% marble) could produce acceptable fibres. The melt viscosities for mixtures 4 (50% slate/50% marble) and 5 (40% slate/60% marble) are too low for good fibre formation. The slate melt which has high viscosities could be converted into fibres by continuous drawing method, which requires much higher melt viscosity than spinning method.

ALKALI-RESISTANCE

Alkali-resistance test results are shown in Table 2 and Figure 9. All six samples provide much higher alkali-resistance than the soda-lime glass. Mixture 2 (70% slate/30 marble) gives the best results but still not as good as high zirconia glass.

Table 2. Alkali-resistance tests

Sample	Wt loss after leaching*	
	6 h	24 h
Slate	1.26	3.97
80% slate/20% marble	1.35	4.25
70% slate/30% marble	1.18	3.47
60% slate/40% marble	1.28	3.72
50% slate/50% marble	1.97	4.25
40% slate/60% marble	2.46	4.81
High zirconia glass	0.55	0.83
Soda-lime glass	4.21	9.43

*expressed in per cent of the original sample weight before leaching test

The Vermont slate-limestone glass fibre was said to exhibit better alkali-resistance than high zirconia fibre (1). The chemical composition for this slate fibre is shown in Table 3 with that for Mix 2 (70% slate/30% marble), the best alkali-resistant glass sample in this study. Mixture 2 is

Table 3. Chemical composition of Vermont slate glass

Sample	Wt %						
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O
Vermont glass	38.6	17.6	4.7	28.0	2.7	2.8	2.2
Mix 2	54.2	12.1	8.1	19.7	1.4	3.1	0.2

significantly higher in SiO_2 and Fe_2O_3 but lower in Al_2O_3, CaO, MgO and Na_2O than the Vermont slate glass. SiO_2 is an acidic oxide that reacts with alkali. The effects of Fe_2O_3, CaO and MgO on the alkali resistance of the Vermont slate glass were also evaluated at UCLA (1). It was found that in general Fe_2O_3 addition reduced alkali resistance and CaO and MgO addition enhanced alkali resistance. Equimolar substitution of Al_2O_3 for Fe_2O_3 in a silicate glass was found to reduce silica extraction in the alkaline region (5). This might be due to the greater passivity of hydrated Al_2O_3 in the alkaline region or to SiO_2 having a lower activity in the Al_2O_3-SiO_2 system than in the Fe_2O_3-SiO_2 system. Less soda was extracted at pH $\geq$ 4 from the glasses containing Al_2O_3 than from those containing Fe_2O_3. Above pH 3 hydrated Al_2O_3 is stable and is known to chemisorb sodium ions. Hydrated iron oxides are also capable of chemisorbing sodium ion, but less effectively. Following the above argument, the combination of higher SiO_2 and Fe_2O_3 and lower Al_2O_3, CaO, and MgO contents could cause the slate glass of this study to show less alkali resistance than the Vermont slate glass.

CONCLUSIONS

The Grenville slate and its mixtures with marble were evaluated as potential charge materials for making alkali-resistant fibres. The melting points for the samples range from 1220 to 1385°C, indicating that they all

should melt easily. The viscosity data show that 3 mixtures (80/20, 70/30, and 60% slate/40% marble) have suitable viscosity range for fibre formation by spinning or blowing method and the slate sample with high viscosities can be converted into fibres by the continuous drawing method. All six glass samples show much higher alkali-resistance than soda-lime glass. The mixture of 70% slate/30% marble gives the best resistance but still lower than the high zirconia glass. Of the six samples the best performance is given by the mixture of 70% slate/30% marble which has the lowest melting point, a suitable viscosity range, and the highest alkali-resistance. However, further experiments are needed to improve alkali-resistance by modifying the chemical compositions, especially by the addition of Al_2O_3.

ACKNOWLEDGEMENT

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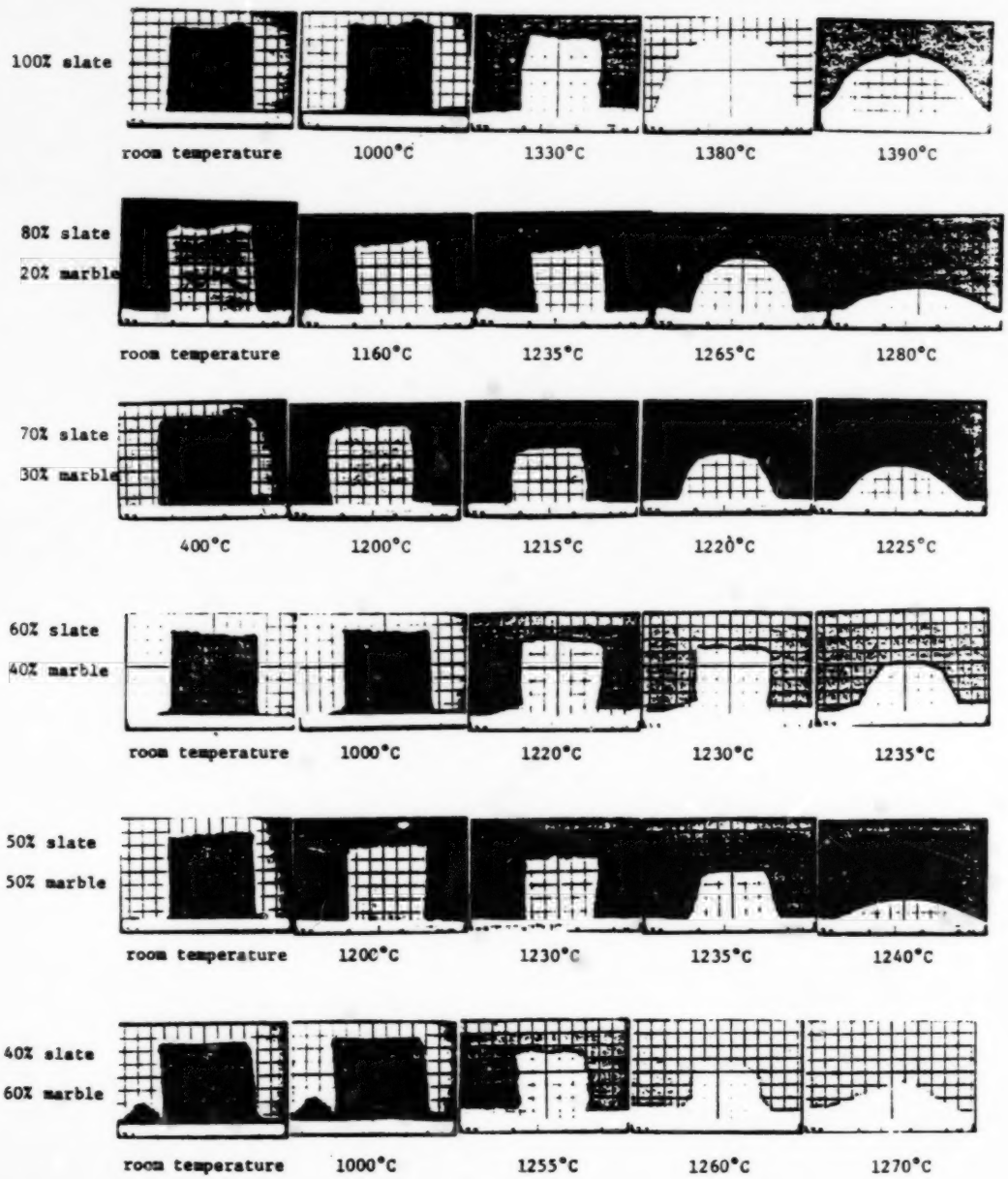

Fig. 1. Series of photomicrographs showing silhouettes of the slate and five mixture samples

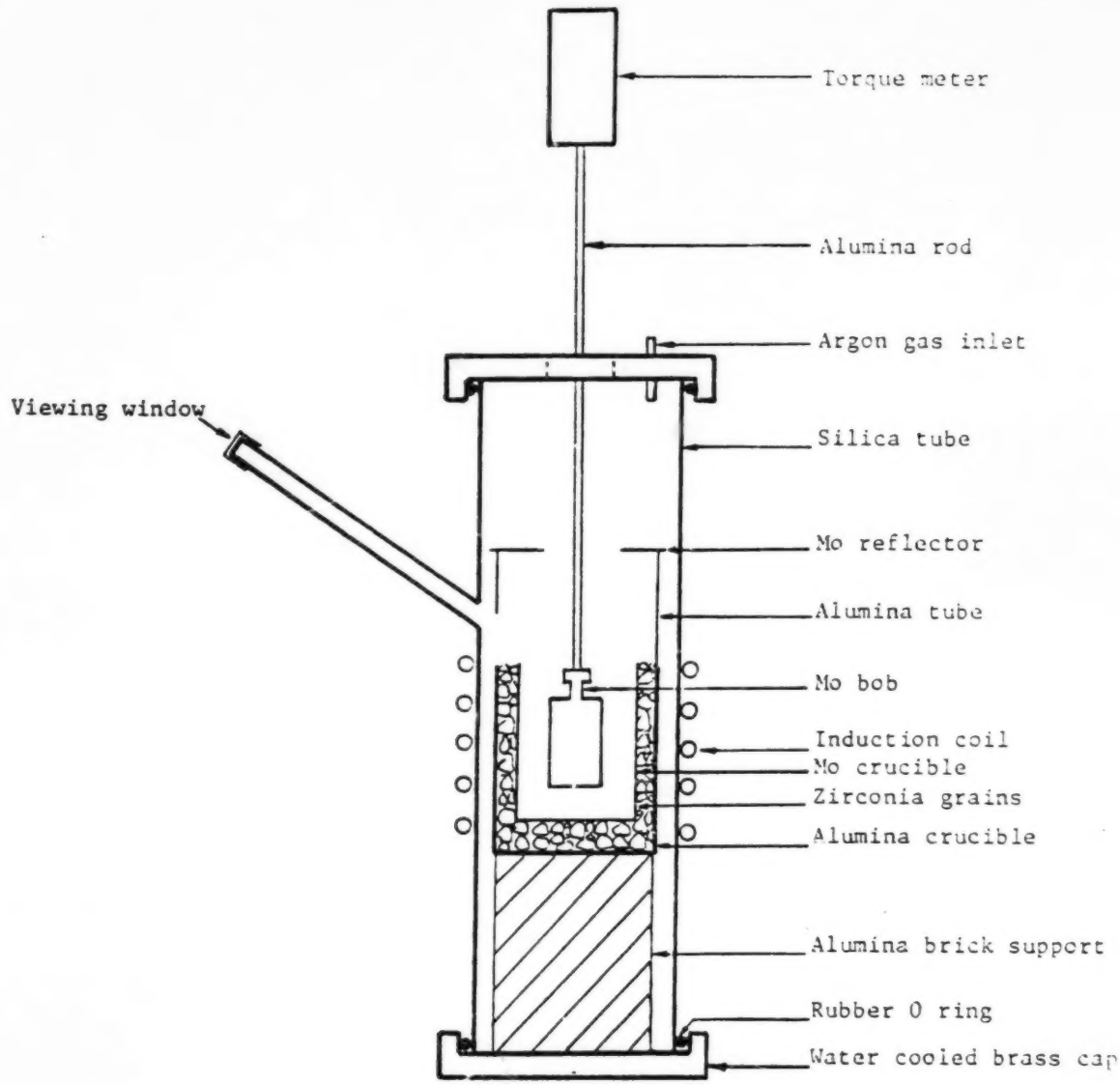

Fig. 2. The viscosmeter set-up

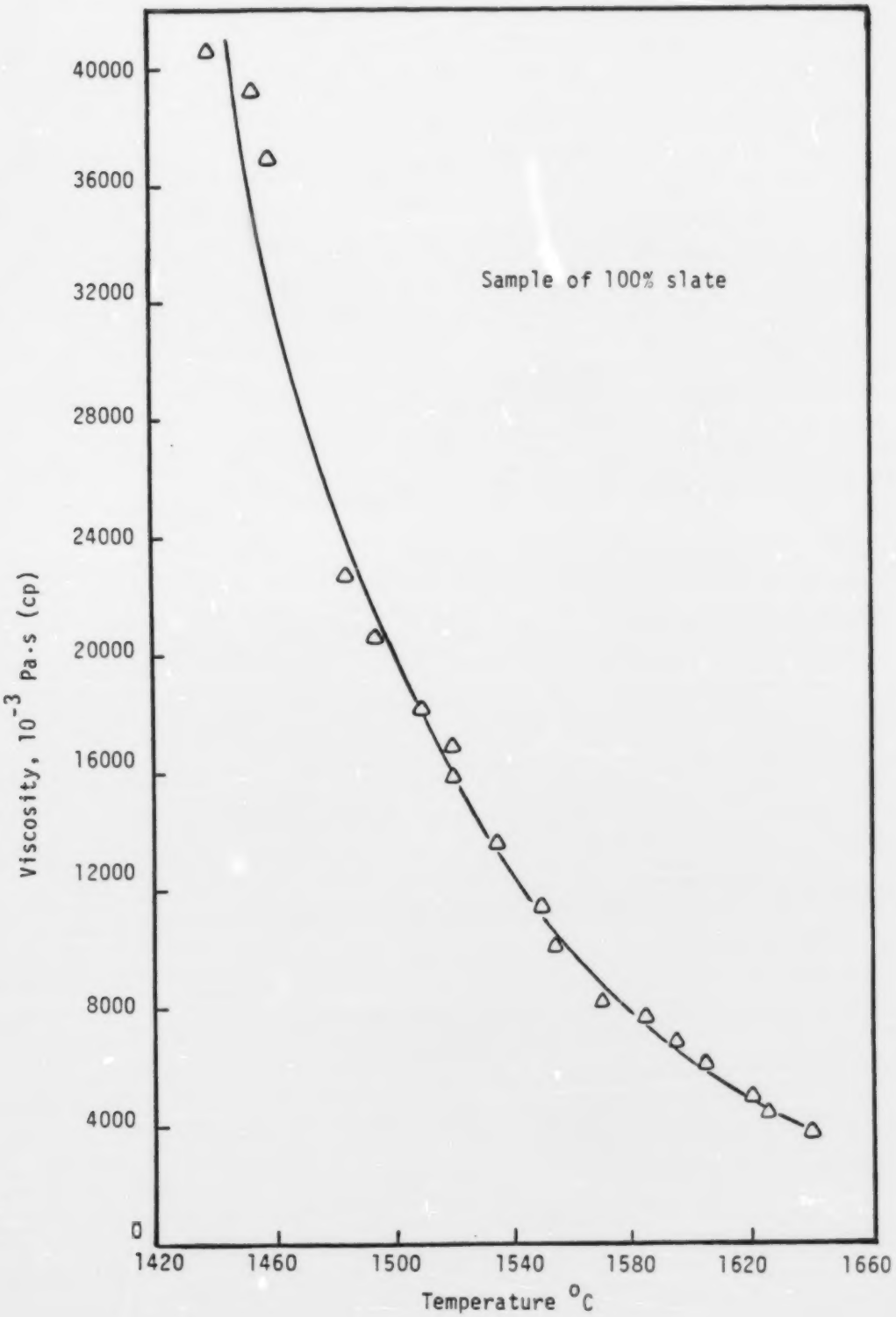

Fig. 3. Viscosity data for slate

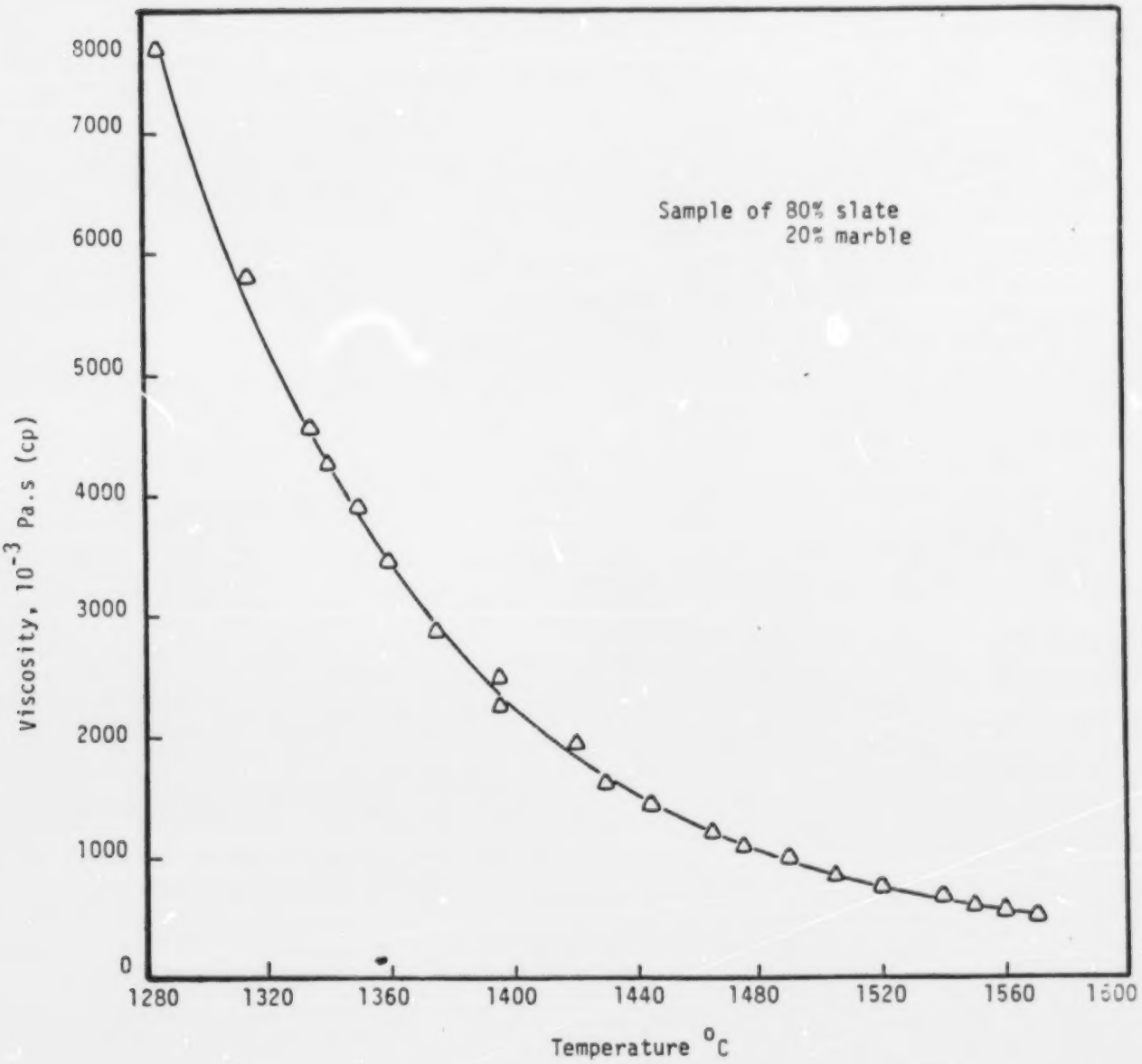

Fig. 4. Viscosity data for Mix 1

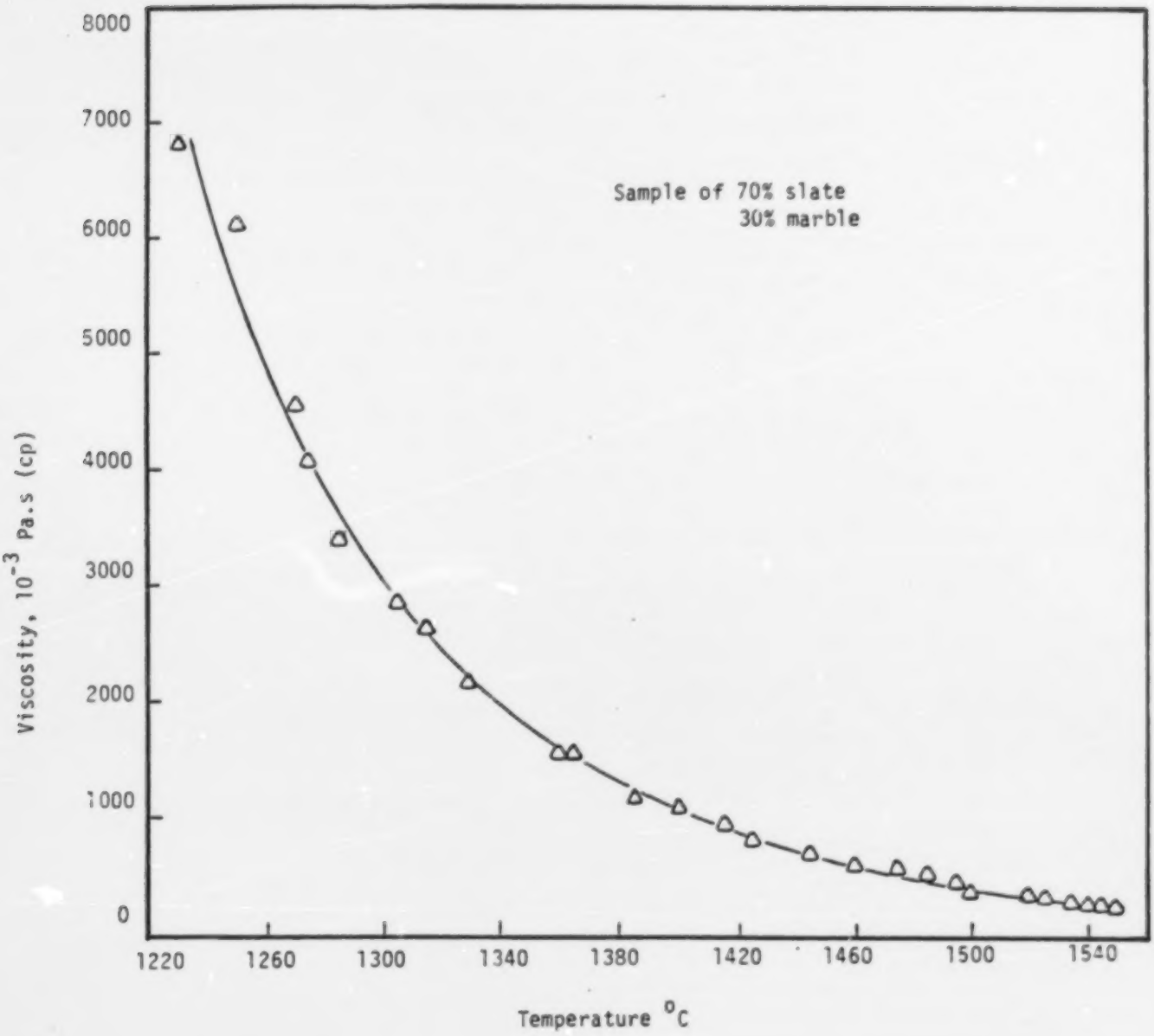

Fig. 5. Viscosity data for Mix 2

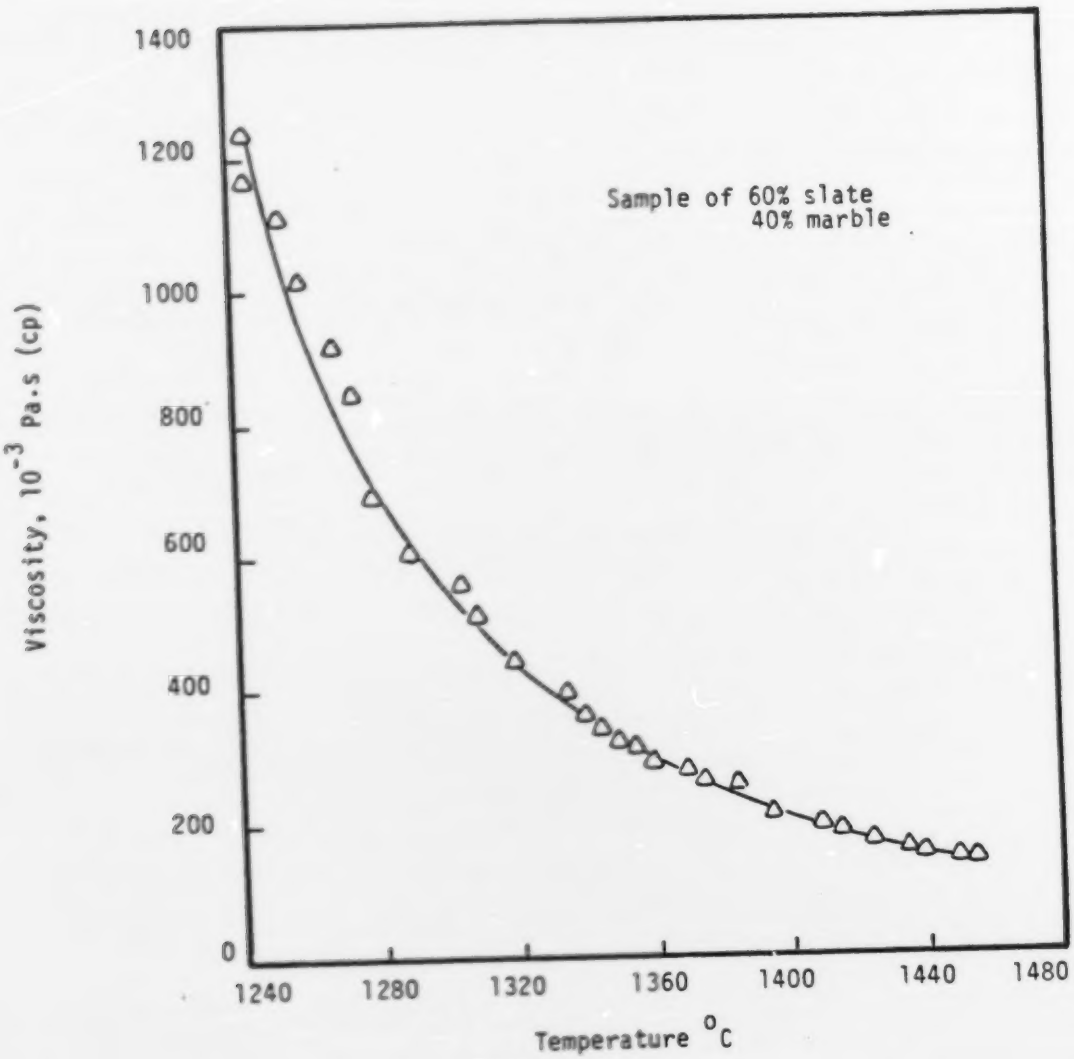

Fig. 6. Viscosity data for Mix 3

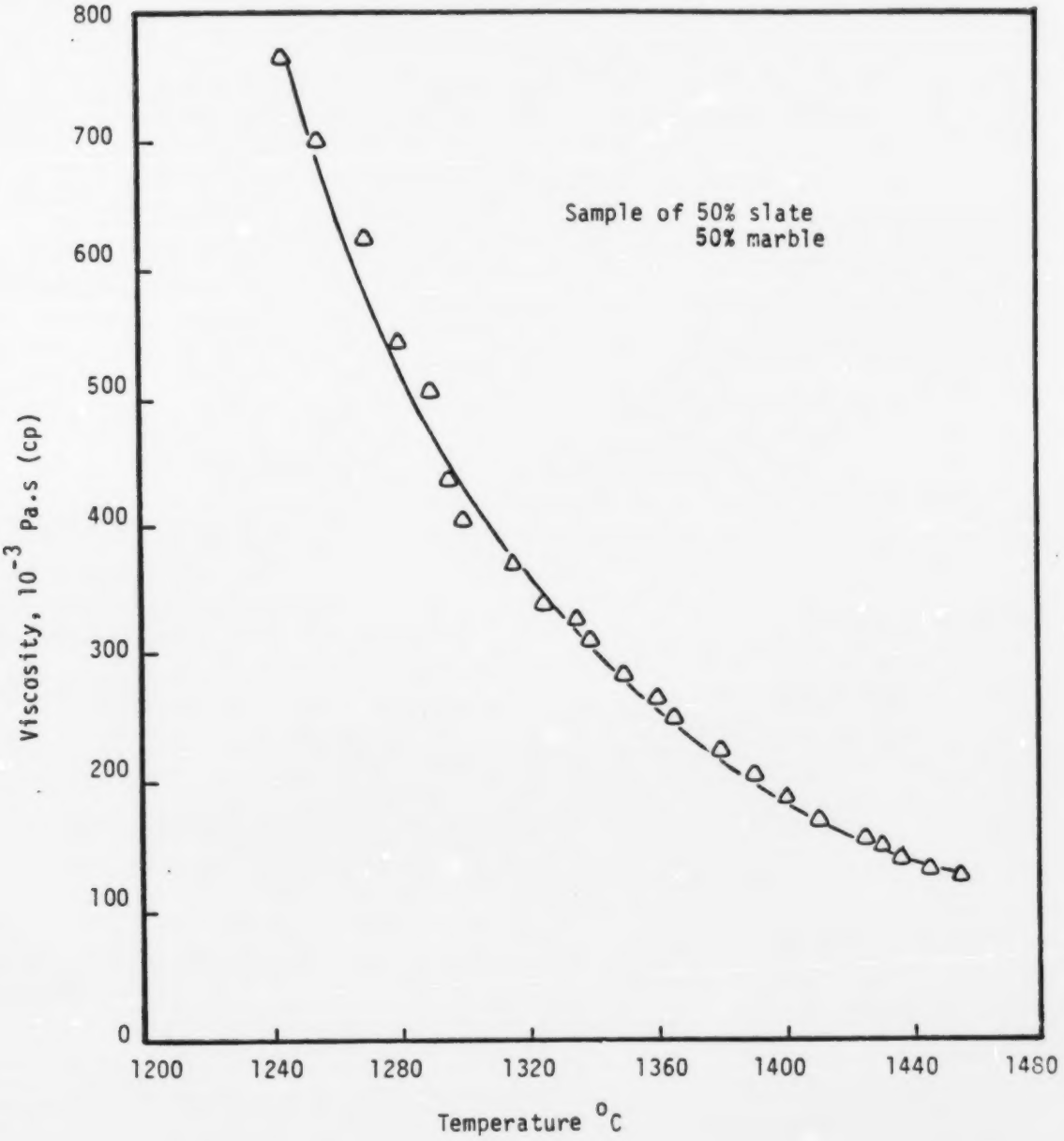

Fig. 7. Viscosity data for Mix 4

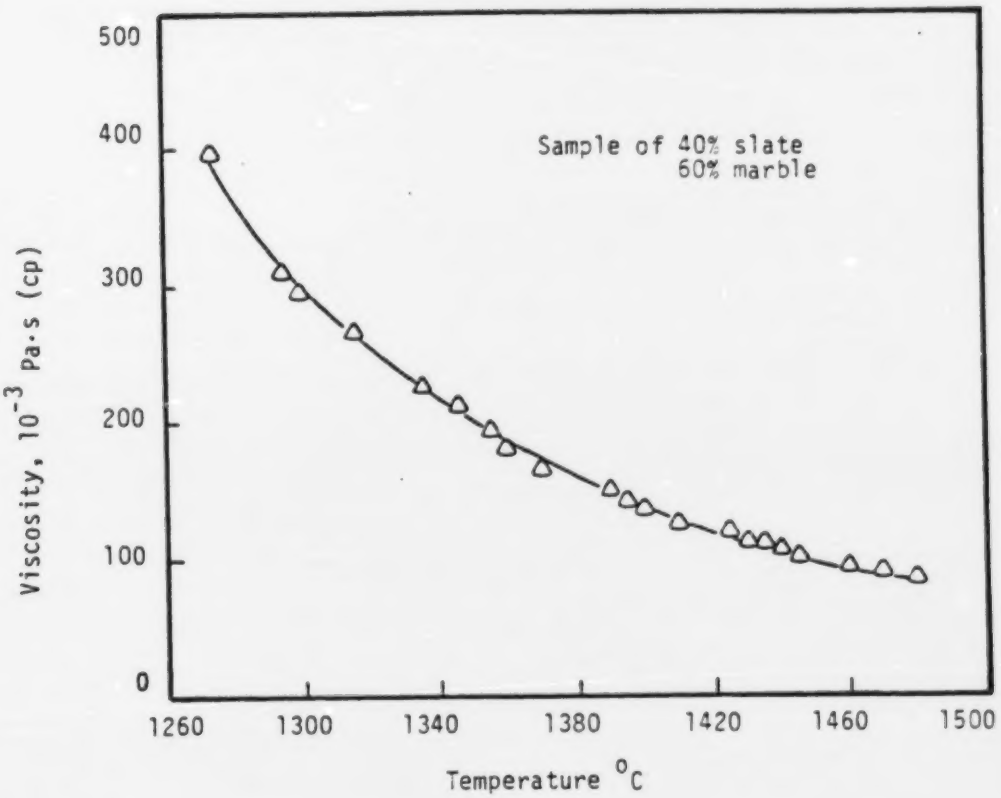

Fig. 8. Viscosity data for Mix 5

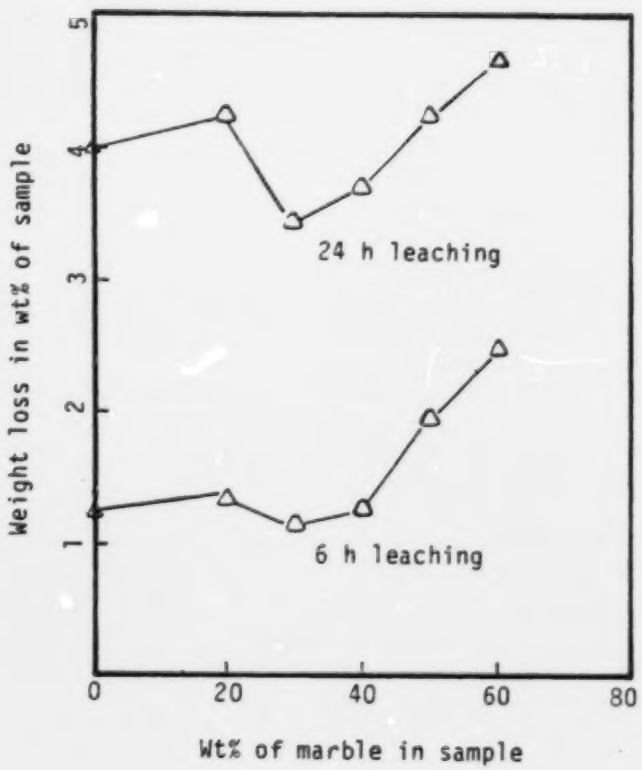

Fig. 9. Alkali-resistance test results for the slate and five mixture samples